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CHARACTERIZATION OF SOLID WASTES FROM LIMESTONE AND RELATED SORBENT INJECTION PROCESSES FOR ACID GAS CONTROL: PHYSICAL AND ENGINEERING PROPERTIES

Report No 88-305-K

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Abstract

A number of tests were conducted to determine the engineering/physical properties of three (two bituminous-derived and one lignite-derived) samples of Furnace Sorbent Injection (FSI) by-product to provide data for the planning of effective FSI waste management. The relatively flat shape of the moisture-density curves indicates that reasonable compaction densities can be achieved with moisture contents below optimum, thus reducing haulage costs of moist FSI by-product. In terms of unconfined compressive strength development and hydraulic conductivity, the slaked FSI materials show equivalent behaviour to that of fly ash generated from similar coal sources.

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To Mr. D.J. Dodd
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Attn: Dr. A. Golomb

CHARACTERIZATION OF SOLID WASTES FROM LIMESTONE AND RELATED SORBENT INJECTION PROCESSES FOR ACID GAS CONTROL: PHYSICAL AND ENGINEERING PROPERTIES

1.0 INTRODUCTION

As part of Ontario Hydro's Acid Gas Control Program, Furnace Sorbent Injection (FSI or LIF) is a candidate technology now considered for installation to control acid gas emissions from thermal generating stations. Furnace injection is a yet commercially unproven process in which the sorbent (limestone or hydrated lime) is injected directly into the furnace of a coal-fired boiler. The FSI reaction by-products, consisting of fly ash, sulphation by-products and unreacted sorbent, is subsequently removed from the flue gas stream using fabric filters or electrostatic precipitators located downstream of the boiler. The volume of FSI by-product is significantly more than from other Flue Gas Desulphurization (FGD) processes because of the high reagent to SO_2 stoichiometry, hence effective waste management of the FSI by-products is of primary concern. With this in view, the specific objective of this study is therefore to determine the engineering/physical properties of FSI waste.

2.0 MATERIAL AND SAMPLE PREPARATION

Three samples of FSI by-product (C1-LV, D1-LV and D13-BD) were supplied by the Chemical Research Department for evaluation. A description of the origin of the three samples is given in Table 1.

Before testing, except for the "as received" moisture content, the FSI material was slaked using deionized water. The slaking procedure consisted of the addition of approximately 1.5 times the stoichiometric equivalent of the molar CaO content in water to the "as received" FSI material (Table 1). The by-product was slaked in batches of 1200 to 1500 g, with initial mixing done manually to ensure even distribution of the water, and completed (4-5 min.) via a Hobart mixer. The mixture was allowed to react for ~30 minutes, stirring occasionally. The final slaked product had the consistency of a dry powder. Once cool the slaked FSI material was stored in a sealed polyethylene container.

3.0 TEST PROCEDURES

Unless otherwise stated, all tests were conducted on slaked samples of the FSI material. The methods used for each of the analyses is given in parentheses immediately following the listed procedure. Whenever possible, standard ASTM test methods were employed. Results for the following tests were obtained:

- -mass increase upon slaking
- -moisture content (as received and after slaking) (ASTM D-2216)
- -specific gravity (ASTM D-854)
- -particle-size distribution by mechanical analysis (ASTM D-451)
- -specific surface area (BET analysis)
- -optimum compacted density (ASTM D-698)
- -porosity at optimum moisture content (by calculation)
- -unconfined compressive strength (ASTM D-2166)
- -freeze/thaw behaviour (ASTM D-560)
- -hydraulic conductivity (coefficient of permeability) (ASTM D-2434)

4.0 RESULTS

4.1 General Physical Characteristics

Table 1 shows the results of some of the physical characterization tests conducted on the FSI samples. Upon slaking, a mass increase occurred as a result of $Ca(OH)_2$ formation. As would be expected, the largest mass increase (8.38%) was determined for the sample having the highest initial CaO content (D1-LV, 290 g CaO/kg FSI). Sample D13-BD, having a very low CaO content of 57.5 $g.kg^{-1}$ material, exhibited a mass increase of 0.55%. The specific gravities of the slaked materials were determined to be 2500 $kg.m^{-3}$, 2470 $kg.m^{-3}$ and 2530 $kg.m^{-3}$ for samples C1-LV, D1-LV and D13-BD respectively.

The grain-size distribution results, as obtained by mechanical analysis, are given in Table 2. Both of the Lakeview TGS samples (C1-LV and D1-LV) had ~95% of the material passing the 0.075 mm (#200) sieve. Seventy six percent of the C1-LV material and 72% of the D1-LV material grains were less than 0.044 mm (passing sieve #325). The Boundary Dam sample visually appeared coarser. The mechanical analysis of its grain-size distribution showed that ~90% of the particles were smaller than 0.075mm and 76% were less than 0.044 mm. The slightly coarser texture of the D13-BD samples is reflected in the measured surface areas as shown in Table 1.

Specific surface areas, as measured by BET (Brunauer-Emmett-Teller) analysis, were determined to be 3.69 $sq\text{-}m.g^{-1}$ for C1-LV, 4.53 $sq\text{-}m.g^{-1}$ for D1-LV and 0.89 $sq\text{-}m.g^{-1}$ for the D13-BD sample.

Table 1

GENERAL PHYSICAL CHARACTERISTICS

Sample	Origin	Sorbent	CaO Content (g/kg)	Slaking Water (gH_2O/kg FSI)	Mass Increase (%)	Moisture Content (%) As Received	Moisture Content (%) Slaked	Specific Gravity (kg/m^3)	Surface Area (sq.m/g)
C1-LV	Lakeview TGS Unit 5 P5, P11, P47	Limestone	235	113	7.48	-0.168*	-0.256*	2500	3.69
D1-LV	Lakeview TGS Unit 5 D1	Slaked Lime	290	150	8.38	.081*	0.845	2470	4.54
D13-BD	Saskatchewan Boundary Dam GS Unit 4	Slaked Lime	57.5	27.7	0.55	-0.004	0.162	2530	0.89

* gained moisture

Table 2

MECHANICAL ANALYSIS OF MATERIAL

C1 - LV (Lakeview G.S., Ont.)

SIEVES	WEIGHT RETAINED	PERCENT RETAINED	PERCENT PASSING
TOTAL (g)	382.53		
40	0.00	0.00	100.00
60	1.62	0.42	99.58
100	3.14	0.82	98.76
140	6.60	1.73	97.03
200	10.04	2.62	94.41
325	69.88	18.27	76.14
PAN	291.25	76.14	0.00

D1 - LV (Lakeview G.S., Ont.)

SIEVES	WEIGHT RETAINED	PERCENT RETAINED	PERCENT PASSING
TOTAL (g)	329.34		
40	0.00	0.00	100.00
60	0.51	0.15	99.85
100	2.38	0.72	99.12
140	4.45	1.35	97.77
200	7.90	2.40	95.37
325	77.53	23.54	71.83
PAN	236.57	71.83	0.00

D13 - BD (Boundary Dam, Sask.)

SIEVES	WEIGHT RETAINED	PERCENT RETAINED	PERCENT PASSING
TOTAL (g)	651.46		
40	1.80	0.28	99.72
60	2.58	0.40	99.33
100	7.25	1.11	98.21
140	15.72	2.41	95.80
200	34.90	5.36	90.44
325	94.30	14.48	75.97
PAN	494.91	75.97	0.00

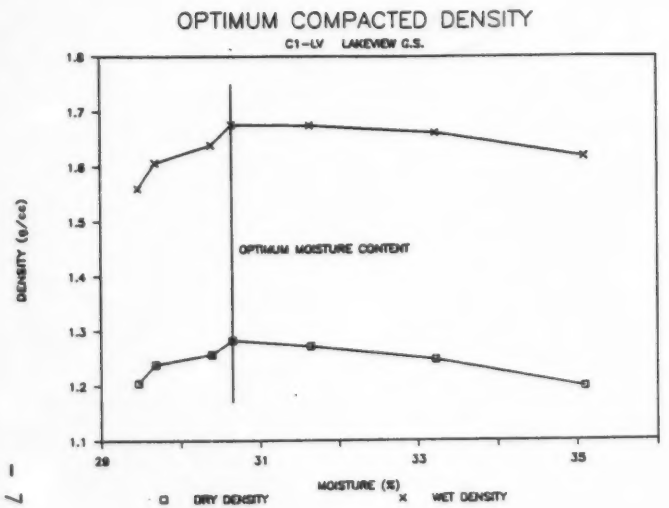
4.2 Maximum Compacted Density

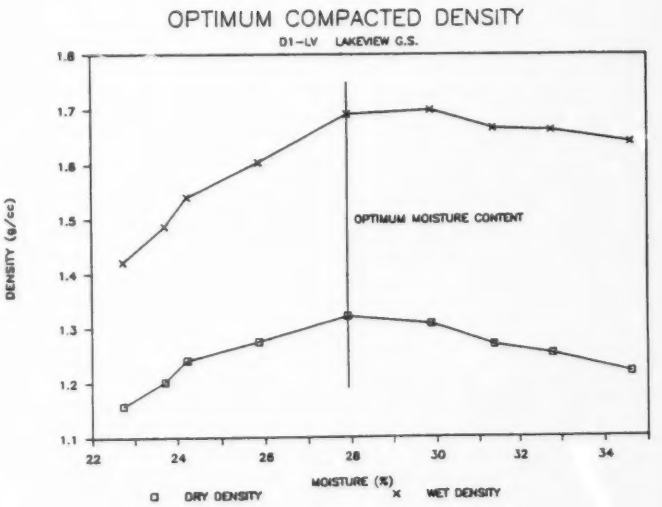
The standard Proctor curves for the slaked FSI samples, as determined by ASTM D-698, are shown in Figure 1. The point of optimum moisture content and maximum dry density (ρ_b) occurred at 30.6% moisture and 1283 $kg.m^{-3}$ for sample C1-LV, 27.9% moisture and 1322 $kg.m^{-3}$ for D1-LV. At a moisture content of 15.1%, the maximum ρ_b of 1625 $kg.m^{-3}$ was determined for sample D13-BD. The shape of the moisture-density curves suggests that the compacted densities obtained are not overly sensitive to small variations in moisture content. This is particularly the case for the D13-BD sample. For example, a 10% decrease in moisture below optimum (15.12% to 13.54%) results in a decrease in dry bulk density of only 1.97%. This relative "insensitivity" to moisture content variations would be of particular significance in landfill operations, as reasonable compaction densities can be achieved with lower moisture contents, thus reducing haulage costs.

4.3 Unconfined Compressive Strength

Unconfined compressive strengths were measured on samples packed at maximum density and aged for 7, 14 and 28 days at 100% humidity and 23°C, according to the ASTM D-2166 standard method. The results are tabulated in Table 3 and the average values for the duplicate results are shown graphically in Figure 2.

From Figure 2, it can be seen that sample D13-BD has a much higher unconfined (u/c) compressive strength after 7 days curing (~2100 kPa) compared with either C1-LV (520 kPa) or D1-LV (270 kPa) and attains its maximum strength of ~2900 kPa after an aging time of 14 days. This maximum attained strength is similar to that of K-Krete or a lightly cemented backfill (Cragg, 1988). In contrast, samples C1-LV and D1-LV do not reach a maximum strength but exhibit increases in u/c compressive strength with time. At 7 days, sample D1-LV developed a strength of ~277 kPa which increased to ~850 kPa after 28 days.





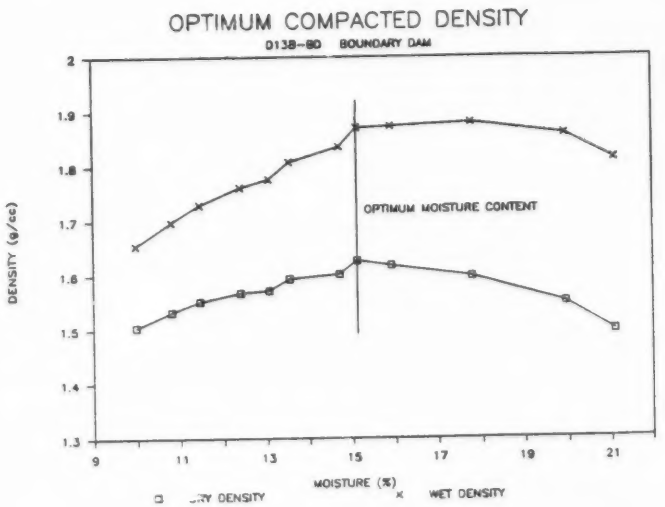


Figure 1 PROCTOR DENSITY CURVES

Table 3

UNCONFINED COMPRESSIVE STRENGTH

	7 DAY					14 DAY					28 DAY				
	DRY BULK DENSITY (kg/m^3)	MOISTURE (%)	LOAD (N)	COMPRESSIVE STRENGTH (kPa)	STRAIN (%)	DRY BULK DENSITY (kg/m^3)	MOISTURE (%)	LOAD (N)	COMPRESSIVE STRENGTH (kPa)	STRAIN (%)	DRY BULK DENSITY (kg/m^3)	MOISTURE (%)	LOAD (N)	COMPRESSIVE STRENGTH (kPa)	STRAIN (%)
D1-LV															
Rep 1	944	30.3	529	290	1.1	971	43.2	630	341	1.8	953	70.5	1556	849	1.4
Rep 2	968	34.7	478	263	0.4	958	40.1	645	354	0.7	968	71.2	1560	853	1.2
C1-LV															
Rep 1	1133	30.4	1030	564	1.1	1134	42.4	1454	798	0.7	1133	56.8	4780	2614	1.2
Rep 2	1134	33.2	864	475	0.5	1132	43.0	1444	794	0.6	1132	53.5	4610	2524	1.1
D13-BD															
Rep 1	1532	15.2	3780	2058	1.6	1554	22.3	5550	3041	1.0	1534	29.2	5370	2940	1.1
Rep 2	1534	18.2	4010	2199	0.9	1545	22.0	5430	2977	0.9	1545	29.3	5440	2974	1.2

NOTE: ASTM (D-2166)
Specimen Size: 4.8 cm diameter; 10.18 cm height

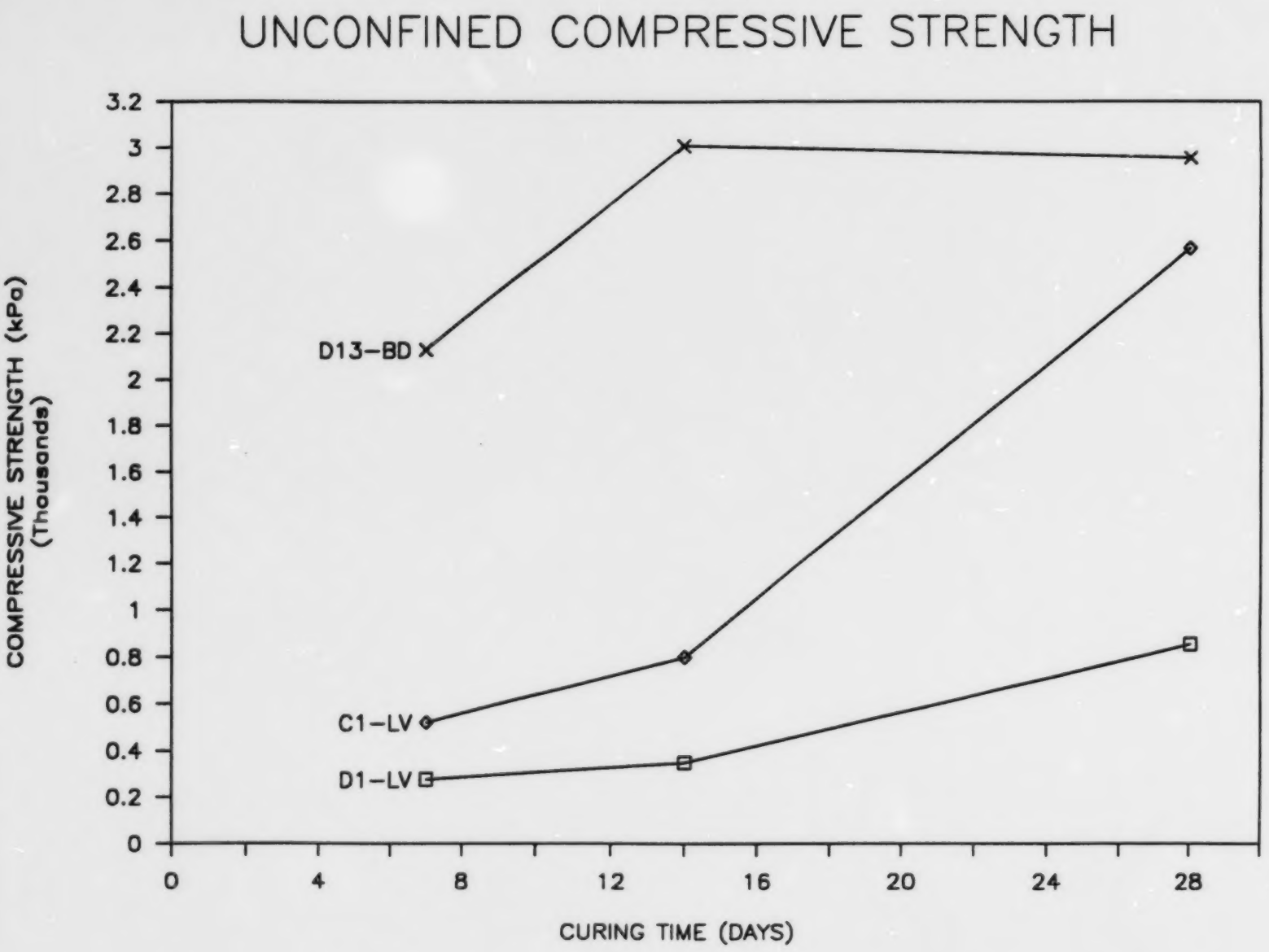


Figure 2 UNCONFINED COMPRESSIVE STRENGTH

The 7 day u/c compressive strength is comparable to very competent soils (ie. hard clay or very dense till). Sample C1-LV attained an initial 7 day strength almost double that of D1-LV and its strength increases dramatically over the 28 day cure period, (~2500 kPa), approaching the high strength attained by sample D13-BD.

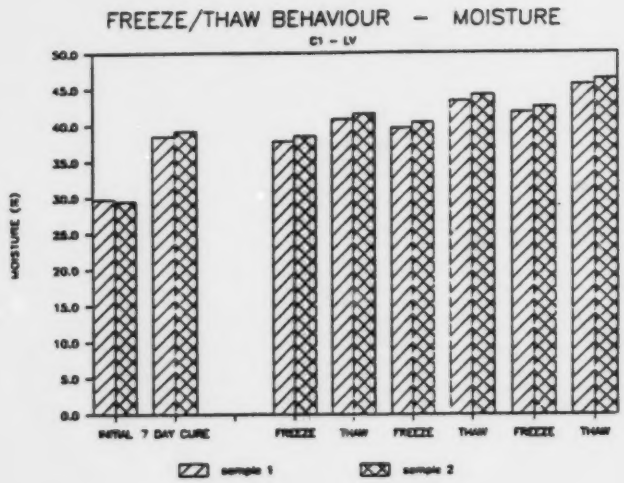
The development of strength in the FSI materials is remarkably similar to that of fly ash generated from bituminous and lignite coals or from lime-amended fly ash (Cragg, 1988). The difference in strength behaviour between the Lakeview TGS' FSI samples and that obtained from Saskatchewan Boundary Dam GS is most probably a function of surface chemical characteristics, D13-BD being produced from a lignite coal while the Lakeview TGS samples were obtained from bituminous coal. The lower unburnt carbon content of the D13-BD sample, combined with the differences in chemistry, is likely also significant.

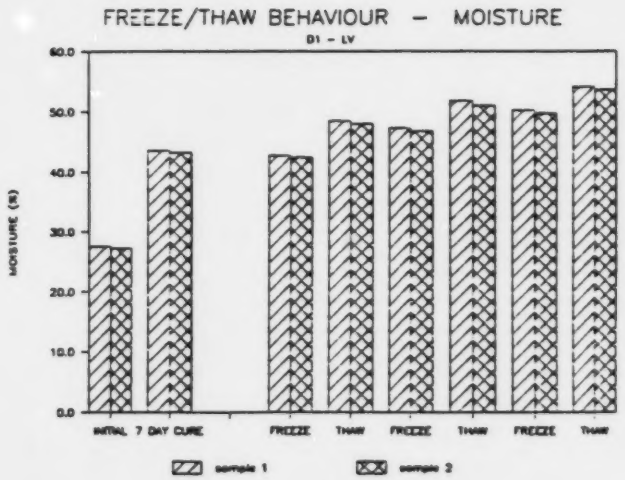
4.4 Freeze/Thaw Behaviour

Stabilized materials such as FSI mixtures may be of use in construction materials such as base or sub-base layers in pavement. In regions where frost action occurs, such as in Canada, these materials must maintain their integrity over time to provide adequate structural performance.

The freeze/thaw behaviour of the three FSI samples were evaluated according to the ASTM D-560 standard procedure for a curing period of 7 days at 100% relative humidity and 23°C. Duplicate tests were performed and samples were initially packed to maximum Proctor bulk density at optimum moisture conditions.

Figure 3 shows the results of the cyclic testing on the moisture content of the samples. Moisture content after curing increased above optimum from 29.6% to 38.8%, 27.4% to 43.4% and 15.4% to 25.7% for samples C1-LV, D1-LV and D13-BD respectively. This corresponds to respective increases of 31.3%, 58.3% and 66.6%. Using the "7 day cure" moisture as a base for comparisons, after





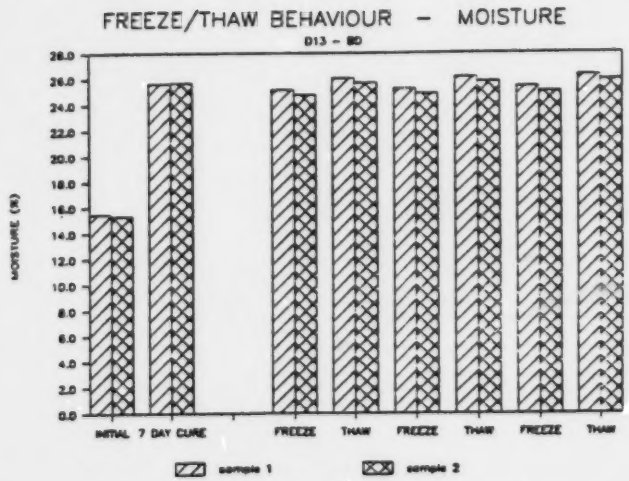


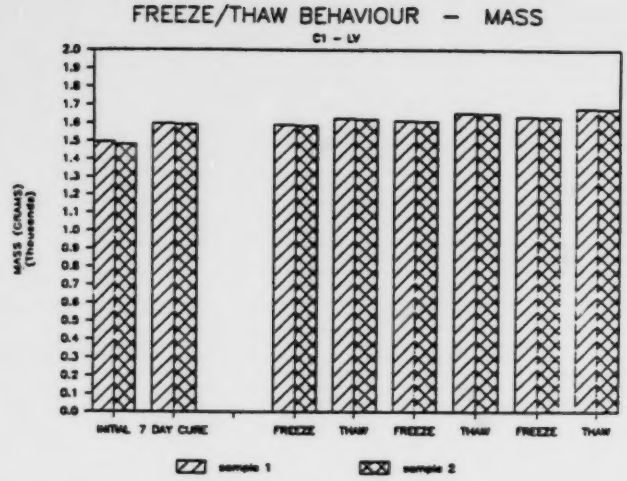
Figure 3 FREEZE/THAW BEHAVIOUR - MOISTURE

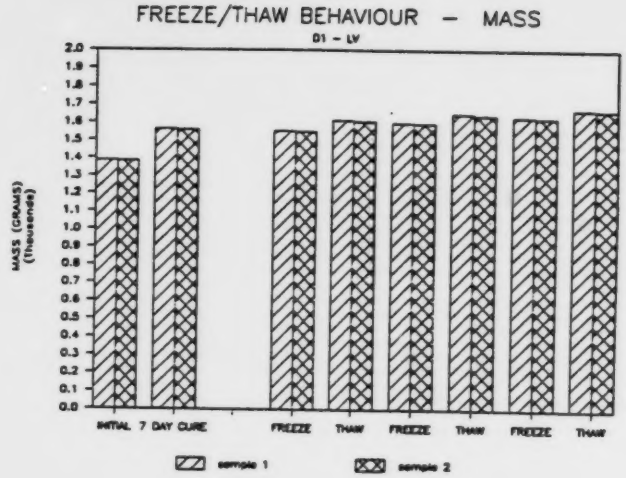
three freeze/thaw cycles, the moisture contents for C1-LV and D1-LV increased gradually to ~46% and 53.9% respectively, corresponding to a total change in moisture content of +18.4% and +24.2%. Sample D13-BD, on the other hand, exhibited only a minor change (<+1.6%) in moisture content (from 25.7% to 26.1%), as shown in Figure 3. The increased water uptake by the bituminous FSI materials may reflect incomplete "cementation" reactions (as seen in strength gain) after 7 days of curing whereas the lignite FSI material has already developed a significant proportion of its strength.

Considering that the total porosities of the samples after the 7 day cure period were approximately 0.48, 0.47 and 0.35 for C1-LV, D1-LV and D13-BD respectively, the results of the freeze/thaw test show that the percent moisture increase for D1-LV exceeded the total available porosity value. That is, the amount of water uptake by D1-LV is more than the volume that would completely fill the void spaces available prior to the test. It also should be noted that the moisture content of C1-LV after the three cycles approached the total porosity capacity of the sample. The Boundary Dam sample, however, remained at ~75% saturation throughout the freeze/thaw cycles.

Observations on the change in mass induced by the freeze/thaw test, parallel those obtained for the moisture content. A mass increase was noted in all three samples following the 7 day cure period with additional increases of 5.2%, 7.4% and 0.3% measured for C1-LV, D1-LV and D13-BD respectively. Again sample D1-LV showed the largest increase in mass while the D13-BD sample exhibited an insignificant mass change (Figure 4).

Changes in volume resulting from the test can be calculated from the dimensional variations shown in Table 4. Here again D1-LV showed the greatest volume change (+12.7%), followed by C1-LV (+6.8%), with the volume of D13-BD remaining essentially constant (+0.57%) throughout the duration of the test. Normally a volume increase of >2% is considered excessive (Catton, 1962).





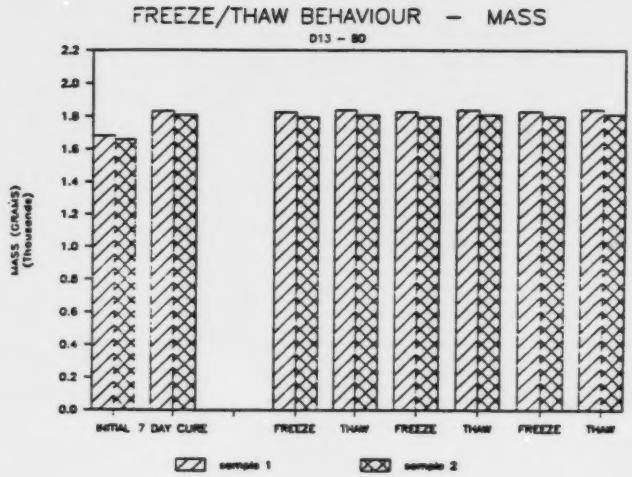


Figure 4 FREEZE/THAW BEHAVIOUR - MASS

Table 4

FREEZE / THAW BEHAVIOUR

Change in Height and Diameter

	C1-LV-1		C1-LV-2	
DIMENSION	HEIGHT	DIAM	HEIGHT	DIAM
INITIAL (mm)	120.0	100.0	120.0	100.0
7 DAY CURE	118.2	102.1	117.0	101.1
FREEZE	119.2	103.1	118.1	102.3
THAW	119.1	102.2	119.2	102.0
FREEZE	120.0	102.0	119.1	102.2
THAW	120.1	102.2	119.1	103.1
FREEZE	120.1	103.6	120.2	103.3
THAW	119.8	103.4	120.1	103.1

	D1-LV-1		D1-LV-2	
DIMENSION	HEIGHT	DIAM	HEIGHT	DIAM
INITIAL (mm)	120.0	100.0	120.0	100.0
7 DAY CURE	116.5	101.0	116.9	101.2
FREEZE	118.5	102.2	118.9	102.1
THAW	118.9	103.1	119.0	102.9
FREEZE	120.8	103.6	121.3	103.9
THAW	120.8	104.1	120.9	104.1
FREEZE	122.5	105.0	122.5	105.0
THAW	122.3	105.0	122.3	105.0

	D13-BD-1		D13-BD-2	
DIMENSION	HEIGHT	DIAM	HEIGHT	DIAM
INITIAL (mm)	120.0	100.0	120.0	100.0
7 DAY CURE	120.1	102.2	119.4	102.0
FREEZE	120.3	103.0	120.0	102.5
THAW	119.0	101.3	118.4	102.0
FREEZE	119.7	102.4	118.9	102.5
THAW	119.0	101.9	119.0	102.0
FREEZE	119.5	102.3	119.3	102.3
THAW	119.3	102.3	119.3	102.3

A detailed visual inspection of the samples was made before, and at the conclusion of the test. The results are given in Table 5. In general, sample C1-LV became somewhat crumbly in appearance while sample D1-LV actually developed very large horizontal fractures which caused breakage. Sample D13-BD however, appeared to retain its integrity. The bituminous FSI material should likely perform better if, prior to the freeze/thaw testing, a longer curing period (ie. 28 to 56 days, which would allow greater strength development) was used.

4.5 Hydraulic Conductivities

Hydraulic conductivity (K) values (coefficient of permeability) were measured for both freshly packed FSI samples and samples that had been cured for 7 days. The ASTM D-2434 standard procedure was used and tests were conducted in duplicate. Results are shown in Table 6.

Hydraulic conductivity values for the freshly packed samples ranged from ~1.1 x 10^{-6} to 1.1 x 10^{-5} $cm.s^{-1}$ with the lowest value occurring in the D13-BD samples and the highest measured for samples C1-LV. These values are typical of those found for low permeability soils such as silt or fly ash.

After aging for 7 days, samples C1-LV and D1-LV showed no change in measured hydraulic conductivity values. However, after curing, the hydraulic conductivity of the Boundary Dam sample (D13-BD) decreased by about half from 1.1 x 10^{-6} $cm.s^{-1}$ to 4.8 x 10^{-7} $cm.s^{-1}$. This decrease in K is mirrored by a reduction in porosity (Table 6) of roughly 3.6%. Porosity changes in the Lakeview samples, on the other hand, were, on average, less than 1%. The decrease in porosity, however, is probably insufficient to cause a decrease in hydraulic conductivity by half an order of magnitude. A redistribution in pore-sizes may also be occurring, with an increase in the number of smaller pore-sizes as curing proceeds. Decreases in hydraulic conductivity similar to those observed for sample D13-BD may occur in the bituminous FSI materials after a longer cure time (ie. 28 to 56 days).

Table 5

FREEZE/THAW BEHAVIOUR - VISUAL DESCRIPTION

AFTER 7 DAYS CURING

C1 - LV	DARK GREY COLOUR MINOR VERTICAL AND HORIZONTAL CRACKS CRUMBLY BOTTOM
D1 - LV	PALE GREY COLOUR MINOR VERTICAL AND HORIZONTAL CRACKS CRUMBLY BOTTOM
D13 - BD	YELLOWISH BEIGE COLOUR MULTIPLE VERTICAL AND HORIZONTAL CRACKS LARGE CHIPS LOOSELY ATTACHED

AFTER 3 FREEZE / THAW CYCLES

C1 - LV	DARK GREY COLOUR NUMEROUS SMALL VERTICAL AND HORIZONTAL CRACKS MANY LARGE VERTICAL AND HORIZONTAL CRACKS BLOCKY APPEARANCE
D1 - LV	PALE GREY COLOUR NUMEROUS SMALL VERTICAL AND HORIZONTAL CRACKS MANY LARGE VERTICAL CRACKS TWO VERY LARGE HORIZONTAL CRACKS BLOCKY APPEARANCE
D13 - BD	YELLOWISH BEIGE COLOUR NUMEROUS SMALL VERTICAL AND HORIZONTAL CRACKS LARGE THIN CHIPS AND SMALL FLAKES LOOSELY ATTACHED

TABLE 6

HYDRAULIC CONDUCTIVITY RESULTS

	FRESH PACKED		7 DAY CURE	
	POROSITY	HYDRAULIC CONDUCTIVITY ($cm.s^{-1}$)	POROSITY	HYDRAULIC CONDUCTIVITY ($cm.s^{-1}$)
C1-LV				
Rep 1	0.489	1.06×10^{-5}	0.483	1.01×10^{-5}
Rep 2		1.04×10^{-5}		1.06×10^{-5}
D1-LV				
Rep 1	0.472	8.46×10^{-6}	0.468	8.68×10^{-6}
Rep 2		8.88×10^{-6}		8.31×10^{-6}
D13-BD				
Rep 1	0.359	1.11×10^{-6}	0.346	4.71×10^{-7}
Rep 2		1.07×10^{-6}		4.99×10^{-7}

5.0 SUMMARY

Physical property and strength tests were conducted on three samples of slaked FSI material. The results of the tests suggest that in general, sample D13-BD to have both greater strength and durability than the C1-LV or D1-LV samples. For examples, neither the C1-LV nor the D1-LV material maintained their physical integrity after undergoing the freeze/thaw testing while sample D13-BD exhibited little change in appearance or moisture/volume conditions. Sample D13-BD also had a slightly higher maximum compacted density which was reflected in the lower measured hydraulic conductivity (K) for this sample. Furthermore, K decreased after the sample had cured for 7 days, while the other samples showed no measurable effect of aging on K value.

Although the initial test results favour the lignite-derived FSI material due to its fast strength gain characteristics, it should be noted that tests performed on the slower strength-attaining bituminous FSI material after a short (7 days) cure period would underestimate its long-term behaviour. This is particularly important for landfill or construction purposes.

6.0 ACKNOWLEDGMENTS

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